

# Search for Streaks in Electron Diffraction Patterns of Strontium Titanate

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Z. Naturforsch. **39a**, 945–947 (1984); received July 11, 1984

Streaks were found in the electron diffraction diagrams of ion-etched single-crystalline  $\text{SrTiO}_3$  for beam incidence parallel to the  $[111]$  direction. The streaks correspond to intensity walls perpendicular to the  $[\zeta 00]$  directions in agreement with the theoretical prediction. The soft phonons seem not to contribute significantly to the streaks.

In the last two decades there have been numerous investigations about the thermal diffuse scattering on substances which undergo some kind of phase transformation, notably ferrodistorsive and antiferrodistorsive phase transformations (see Dorner and Comès [1]). In these studies neutron and X-ray scattering techniques have been used. Electron scattering can be in principle used to arrive at similar results, although dynamical effects might cause difficulties in the interpretation of the scattering patterns. Strontium titanate represents a special case, the fluorescence of the strontium atoms obscures the observation of the diffuse X-ray scattering. Hence there are only few studies of the structure of  $\text{SrTiO}_3$  by X-ray diffraction (Fujishita, Shiozaki, and Sawaguchi [2], Lytle [3]). To our knowledge neither a study of thermal diffuse scattering nor an analysis of streaks in the electron diffraction diagram of strontium titanate have been reported in the literature.

Electron scattering studies on various perovskite crystals (for example on  $\text{BaTiO}_3$ ) have been carried out by Honjo, Koderä, and Kitamura [4]. The observed streaks, which appear through the inelastic electron-phonon scattering, could be explained using the concept of intensity walls (Honjo et al. [4], Dorner and Comès [1], see also Cochran [5]). The differential cross section for the inelastic scattering under participation of phonons is in the

Debye approximation proportional to  $\omega^{-2}$ , where  $\omega$  is the phonon frequency. This means, low-energy phonons are favored. The momentum transfer of the scattered electron selects the polarisation of the phonons.

In the course of the present investigations electron scattering diagrams of silicon single crystals were obtained showing streaks, which could be explained in terms of intensity walls perpendicular to  $[\zeta \zeta 0]$ , in agreement with the results of Honjo et al. [4]. The streaks in our electron scattering diagrams of barium titanate could be explained likewise through intensity walls perpendicular to  $[\zeta 00]$  (Figure 1). The phonon dispersion curves show phonons with very low frequencies, which propagate in the direction  $[\zeta \zeta 0]$  in Si (Price, Sinha, and Gupta [6]) and in the direction  $[\zeta 00]$  in  $\text{BaTiO}_3$  (Shirane et al. [7]). This is consistent with the idea mentioned above, that cross sections for thermal diffuse scattering involving low-frequency phonons are in general large. Note, that Fig. 1b shows streaks in the electron diffraction diagram of  $\text{BaTiO}_3$  for  $[111]$  incidence, where Honjo et al. [4] found the streak intensity to become vanishingly weak.

Strontium titanate has a very high phonon density of states near 3 THz (Stirling [8]), which should give rise to thermal diffuse scattering. The frequencies of the soft mode at the  $\Gamma$ -point were reported (Migoni, Bilz, and Bäuerle [9]) as 2.7 THz at 300 K and 1.7 THz at 135 K. The frequencies at the  $R$ -point are 1.6 THz and 0.16 THz, respectively (Bruce and Cowley [10]). The question arises whether these soft modes or other low-frequency phonons could cause streaks in the electron scattering diagrams of strontium titanate.

In order to obtain single-crystalline samples, oriented platelets were cut perpendicular to the

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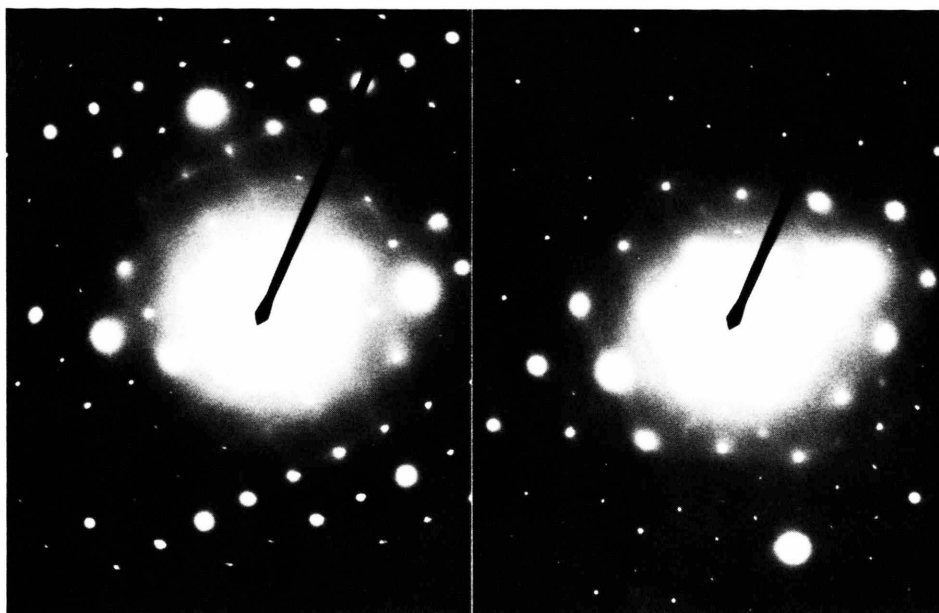


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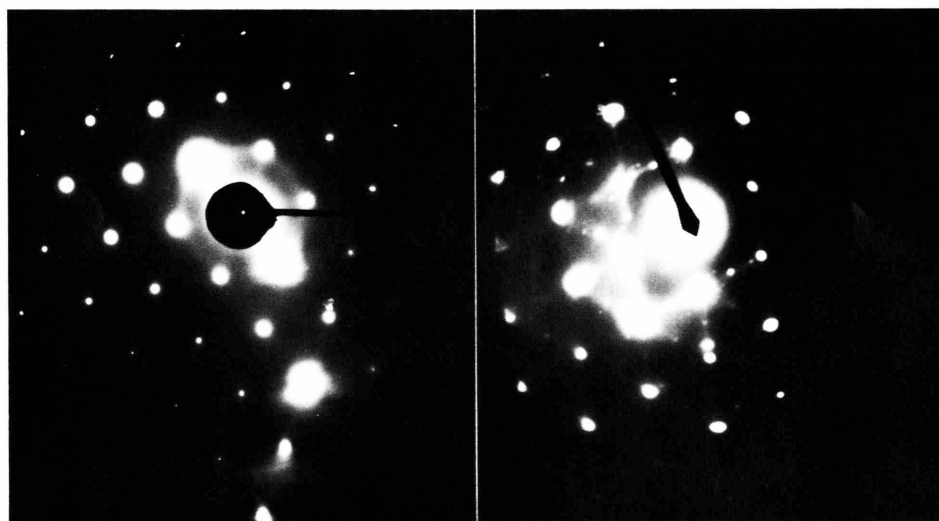
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a)

b)

Fig. 1. Streaks in the electron diffraction diagram of  $\text{BaTiO}_3$ , beam parallel to  $[100]$  (a) and to  $[111]$  (b), primary energy 200 keV, room temperature. Streaks correspond to intensity walls perpendicular to  $[\zeta 00]$  directions in both diagrams.



a)

b)

Fig. 2. Streaks in the electron diffraction diagram of  $\text{SrTiO}_3$ , beam parallel to  $[111]$ , primary energy 100 keV (a) and 200 keV (b), room temperature.

principal directions  $[100]$ ,  $[110]$  and  $[111]$  from a strontium titanate bowle, supplied from Titanium Pigments Inc. The platelets were polished with diamond paste down to a thickness of  $50\text{ }\mu\text{m}$  and then thinned from both sides with 6 keV argon ions.

Scattering diagrams were obtained at room temperature with 200 keV electrons and at probe temperatures between 135 and 300 K with 100 keV electrons (Figure 2). The high quality of the single-crystalline samples was ensured through observation

of Kikuchi lines which had a width of about 0.6 mrad.

The streaks observed in Fig. 2 run in directions which correspond to intensity walls perpendicular to the propagation directions  $[\zeta 00]$  for the low-frequency phonons involved. Stirling [8] proposed models for the crystal dynamics of SrTiO<sub>3</sub> which lead to  $[\zeta 00]$  intensity walls although the anisotropy of the dispersion surface is relatively weak. This orientation of the intensity walls agrees with the present result. According to these models [8], the transverse acoustic phonon branch in the direction  $[\zeta 00]$  shows particularly low energies. It is this branch which is most likely responsible for the appearance of the streaks. The effect of low-frequency phonons with high momentum is visible in the diffraction pattern as extra spots which do not belong to the reciprocal lattice (Figure 2).

The contribution of the soft modes to the thermal diffuse scattering has to be considered in relation to temperature changes. A decrease of the phonon frequency near the phase transition temperature should be visible as an increase of the diffuse intensity. No measurable increase in the scattered intensity was observed when the samples were cooled down to 135 K. Therefore, contrary to the

behaviour in BaTiO<sub>3</sub> and in other ferroelectric perovskites, the soft modes in strontium titanate do not seem to contribute noticeably to the streaks in the temperature region investigated, because they do not cause such a strong perturbation of the crystal structure as e.g. in BaTiO<sub>3</sub>.

It must be mentioned that the streaks were not always observed. Only samples cut perpendicular to  $[111]$  showed streaks in selected areas. This can be explained by the high sensitivity of the phonon frequencies of SrTiO<sub>3</sub> to defects such as changes in composition; note ion-etching produces a strontium-rich structure\*. On the other hand, Kikuchi lines are not so sensitive. They are observed on all samples of suitable thickness for any orientation.

#### Acknowledgements

We thank Dr. K. Smidoda (Institut für Werkstoffkunde, Universität des Saarlandes) for his great help with the 200 kV electron microscope. G. A. also thanks for a grant from GTZ-DAAD.

\* Previous investigation in this laboratory showed that chemically thinned samples perpendicular to  $[100]$  gave streaks with  $[\zeta 00]$  orientation, too (E. Ockenfuß).

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